
A Review on PZT-Polymer Composites: Dielectric and Piezoelectric Properties

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ABSTRACT

Ferroelectric materials exhibit piezoelectric natures. In this work, PZT is selected as the prime component and the polymers which exhibit few piezoelectric properties are selected. This paper reviews for the different polymers like PVDF, PVC, PU, P(VDF-TrFE) and Polyester resin. The composite obtained by the individual polymer with PZT is used for transducer applications and accelerometers. The various methods selected for the composites have been reviewed as reported from literatures. The thorough study on the composite revealed that volume fraction, temperature, particle size of PZT affects the dielectric and piezoelectric properties. There is an increase in the dielectric properties and piezoelectric properties when the parameters like volume fraction, temperature, particle size increase in their respective dimensions.

Keywords: Ferroelectric, polymers, accelerometer, dielectric, piezoelectric properties.

INTRODUCTION

Ferroelectric materials exhibit excellent piezoelectric properties. Single phase pure ceramics like PZT, BaTiO₃, PMN, PMN-PT have high dielectric

constant, piezoelectric strain coefficient, high curing temperature, low piezoelectric voltage coefficient and low dielectric loss. They have high acoustic impedance which did not match with water and human tissues. High density and stiffness makes them less

compliant. Their high acoustic impedance and lack of flexibility restricts their applications¹⁻⁶. In this study PZT alone is selected to understand the properties of ceramic-polymer composite.

On the other hand polymers like PVDF (Polyvinylidene Fluoride), PVC (Polyvinyl Chloride), PU(Polyurethane) and copolymers like P(VDF-TrFE) exhibit few piezoelectric properties. Polymers have low relative permittivity, low piezoelectric strain coefficient, high piezoelectric voltage coefficient, low acoustic impedance and very high enough flexibility when compared with pure ceramics. Even though they have low electrical properties their mechanical properties are the main reason to fabricate the composite. In the composite superior electro active properties of the ceramics and mechanical properties of the polymers are combined together⁹. In composites dielectric constant, piezoelectric strain coefficient d_{33} , acoustic impedance and density all parameters relatively reduced and required compliance is achieved. Pure PZT is brittle and not flexible enough to suit in a curved surface or in any irregular shapes. But the composites can be made in any required shape. Polymers like PVDF, PVC, P(VDF-TrFE), PU, epoxy, polyester resin are used to fabricate composites^{7,18-20,38-51}. In this study the PZT-Polymer composites have been selected for the review. One of the important phenomena in the preparation of the composites is “connectivity”. The name connectivity was first introduced by Newnham *et al.*¹⁰. He reported that for the diphasic composites, there are 10 possible connectivities (0-0, 0-1, 0-2, 0-3, 1-1, 1-2, 1-3, 2-2, 2-3, 3-3). Among all the connectivity patterns 0-3 connectivity is the most often

used and uncomplicated connectivity. In this type of connectivity, ceramic inclusions are randomly dispersed in the polymer matrix. In 0-3 connectivity there is no particle-particle contact of the ceramic inclusions and polymer has a three dimensional connection^{11,12}. In this work, only 0-3 connectivity has been selected to study composites mentioned.

Most advantage of the composites over pure ceramics is piezoelectric or pyroelectric property can be suppressed. That is in monolithic ferroelectric materials, pyroelectric activity cannot be achieved without piezoelectric activity, but it is only possible in composites¹³. Particle size of ceramic inclusion, poling methods, temperature, volumetric percentage, preparation methods are important aspects affecting the dielectric and piezoelectric properties¹⁹⁻³⁰. In this study the various polymers were compared and analysed for their dielectric and piezoelectric properties. Composites can be used in variety of applications like sensors, accelerometers, hydrophones, sonars, medical imaging and also in high energy storage capacitances^{7,14-16}. Composites can be tailored for suitable applications. In this study the various polymers used with PZT could be mostly for accelerometer and transducer applications.

2. MATERIALS AND METHODS

A number of methods exist to prepare the PZT-Polymer composites of 0-3 connectivity like solvent casting, colloidal, spin coating, flow extension method, hot press method, cold press method, centrifuge method and tape casting method. The properties of various composites obtained by various methods are reported in the

literatures^{7,18-20,22,23,26,27,38-51}. In this review paper, all the methods could not be brought into this text.

3. RESULTS AND DISCUSSION

3.1. Dielectric properties

3.1.1. Dielectric constants

Many numbers of equations are available in literature for finding the ceramic inclusion concentration dependent variation in effective relative permittivity of the composite. Shapes of the ceramic inclusion also make sense while choosing correct equation. Bruggeman model or modified effective medium theory (EMT) equation. Dias–Dasgupta equation using Yamada model^{7,17}.

$$\varepsilon_{eff} = \varepsilon_B \left[1 + \frac{f_A(\varepsilon_A - \varepsilon_B)}{\varepsilon_B + n(1 - f_A)(\varepsilon_A - \varepsilon_B)} \right] \rightarrow \quad (1)$$

Where, n is the morphology factor, ε is the relative permittivity, f_A is volume fraction of the inclusion. The subscripts A and B represent the polymer and ceramic respectively. In this model particles are assumed to be ellipsoidal in shape and dispersed in the continuous medium.

Analytical models are suited with experimental results only in lower volumetric percentages. After that discrepancy increases with the theoretical models¹⁸. The dielectric constant increases with the increase PZT volume percentage^{16,19-22,25,26,28,30}. This is due to the contribution of PZT in the electrical properties of the composite. Figure.1 shows change in permittivity with change in volume percentage of PZT in PZT-P(VDF-TrFE) composite. Particle grain size of the ceramic inclusion will also affects the relative permittivity of the composite³⁵. Increases in particle grain size of PZT will increase the permittivity. Polarity of the

polymer matrix and temperature also affects the permittivity. Increase in temperature increases the permittivity^{20,21,26,30}. Figure.2 shows the variation of permittivity with respect to change in temperature. This is because higher orientational polarization of the polymer matrix at higher temperatures causes by greater mobility of molecules²⁰. Increase in frequency decreases the relative permittivity^{8,29,30,32-34}.

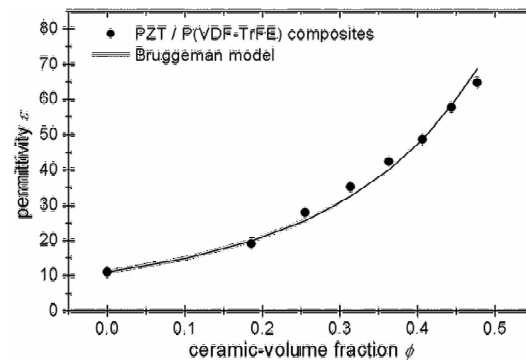


Figure1. Change in permittivity with the increase of PZT volume fraction for PZT / P(VDFTrFE) composites²⁵. Solid line represents the theoretical value calculated using Bruggeman model.

For better contribution to the electrical and vibrational aspects the higher permittivity is required. The increase in poling field increases the dielectric constant³⁶. For same volume fraction various researchers reported different permittivity for the same composite^{18-20,26,27,39,41,48}. This is due to their different preparation method^{19,20}, poling method^{7,13,27}, particle size^{22,35}, temperature^{20,21,26,30} and frequency^{9,29,30,8,32,34}. A polymer with high permittivity used in the composite also increases the permittivity. Adding a third phase material like carbon also affects the permittivity^{33,34}. Maximum value obtained experimentally for the composites are still much smaller than the pure ceramics. Yamada *et al.*⁷ reported

higher relative permittivity for PZT-PVDF composite with the value of 152. Relative permittivity values for different composites are shown in Table1.

Table1: Dielectric and piezoelectric properties of PZT-PVDF Composites.

| Host | PZT Vol% | ϵ_r | d_{33} (pC/N) | g_{33} (10-Vm/N) | $\tan \delta$ | FOM _{piezo} (10-12m 2/N) | Ref |
|-----------------|----------|--------------|-----------------|--------------------|---------------|-----------------------------------|------|
| PVDF | 10 | 9.84 | 4 | 45 | 0.025 | 0.180 | [39] |
| PVDF | 30 | 12.57 | 4 | 36 | 0.040 | 0.144 | [39] |
| PVDF | 50 | 96.8 | 13.8 | 16.1 | | 0.222 | [20] |
| PVDF | 50 | 68.1 | 14 | 24.99 | 0.0198 | 0.349 | [34] |
| PVDF | 50 | 56 | 14 | 28 | 0.0055 | 0.392 | [41] |
| PVDF | 50 | 18.09 | 4 | 25 | 0.042 | 0.100 | [39] |
| PVDF | 55 | 120 | 130 | 122.5 | | 15.925 | [23] |
| PVDF | 60 | 94.48 | | | | | [42] |
| PVDF | 65 | 45 | 33 | 82.8 | | 2.732 | [40] |
| PVDF | 67 | 152 | 48.3 | 35 | | 1.690 | [7] |
| PVDF | 70 | 82.6 | 41 | 56.0 | | 2.296 | [19] |
| PVDF | 70 | 35.96 | 5 | 15.7 | 0.040 | 0.078 | [39] |
| PVDF | 70 | 140 | | | 0.3 | | [48] |
| PVDF | 80 | | 95 | 125 | | 11.785 | [51] |
| PVDF | 90 | 126.5 | 16 | 14.2 | 0.045 | 0.227 | [39] |
| PVC | 30 | 8.61 | 4.0 | 52.49 | | 0.210 | [38] |
| PVC | 40 | 25.06 | 6.0 | 27.06 | | 0.16 | [38] |
| PVC | 40 | 29.5 | | | | | [43] |
| PVC | 50 | 43.7 | 13.0 | 33.61 | 0.0202 | 0.436 | [34] |
| PVC | 50 | 39.30 | 15.0 | 43.18 | | 0.64 | [38] |
| PVC | 60 | 73.11 | 22.0 | 34.50 | | 0.78 | [38] |
| PVC | 60 | 134 | 29.0 | 24.0 | 0.23 | 0.70 | [44] |
| PVC | 70 | 97.78 | 31.0 | 35.41 | | 1.10 | [38] |
| P(VDF-TrFE) | 15 | 16.8 | 2.2 | 14.7 | | 0.032 | [47] |
| P(VDF-TrFE) | 20 | 35 | | | 0.033 | | [18] |
| P(VDF-TrFE) | 24 | 20.5 | 5.3 | 29.1 | | 0.154 | [47] |
| P(VDF-TrFE) | 30 | 45 | | | 0.032 | | [18] |
| P(VDF-TrFE) | 30 | 27.6 | 20 | | | | [26] |
| P(VDF-TrFE) | 35 | 33.4 | 10.2 | 34.4 | | 0.351 | [47] |
| P(VDF-TrFE) | 40 | 65 | | | 0.026 | | [18] |
| P(VDF-TrFE) | 45 | 52 | 18.9 | 41.0 | | 0.775 | [47] |
| P(VDF-TrFE) | 50 | 72 | | | 0.023 | | [18] |
| P(VDF-TrFE) | 50 | 70.2 | 21.0 | 33.4 | | 0.701 | [26] |
| P(VDF-TrFE) | 50 | 118 | | | 0.02 | | [27] |
| P(VDF-TrFE) | 51 | 72 | 23.0 | 36.1 | | 0.830 | [47] |
| P(VDF-TrFE) | 60 | 124.2 | 42 | 38.2 | | 1.604 | [26] |
| Polyurethane | 11 | 8.3 | | | | | [46] |
| Polyurethane | 15 | 10.3 | | | | | [46] |
| Polyurethane | 19 | 21 | | | | | [46] |
| Polyurethane | 19 | | 14.9 | | 0.53 | | [29] |
| Polyurethane | 32 | 24 | | | | | [46] |
| Polyurethane | 50 | | 13 | | | | [32] |
| Polyurethane | 60 | 51±5 | 25±5 | | 0.02 | | [45] |
| Polyurethane | 70 | 45±5 | 28±5 | | 0.04 | | [45] |
| Epoxy | 40 | 110.0 | | | 0.017 | | [49] |
| Epoxy | 70 | 76.1 | 1.6 | 2.37 | | 0.004 | [50] |
| Polyester resin | 40 | 45 | 10 | 25 | 0.0140 | 0.251 | [22] |
| Polyester resin | 50 | 52 | 18 | 39 | 0.0138 | 0.703 | [22] |
| Polyester resin | 60 | 84 | 26 | 34 | 0.0141 | 0.908 | [22] |
| Polyester resin | 65 | 88 | 29 | 37 | 0.0353 | 1.079 | [22] |

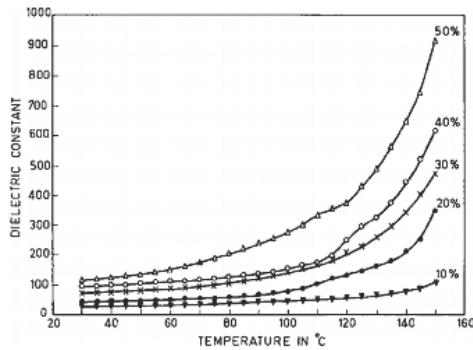


Figure.2. Variation of dielectric constant with temperature in PZT-PVDF Composite for different volume percentage of PZT²⁰.

3. 1. 2. Dielectric loss factor

The filler concentration dependent variation of effective dielectric loss of the composite is shown below³¹

$$\epsilon_{eff}'' = \epsilon'' = \frac{\epsilon_p''[(\epsilon_c' - \epsilon_p')(\epsilon_c' + 2\epsilon_p')\epsilon_p']}{[(\epsilon_c' - \epsilon_p')(\epsilon_c' + 2\epsilon_p')\epsilon_p']} + \epsilon_c'' \frac{3(\epsilon_c' - \epsilon_p')\epsilon_p'}{(\epsilon_c' - \epsilon_p')(\epsilon_c' + 2\epsilon_p')} \rightarrow \quad (2a)$$

ϵ' and ϵ'' are the real and imaginary parts of permittivity. The suffix c, p represents the ceramic and polymer respectively. The $\tan \delta$ is the loss tangent. The parameters like particle grain size, shape of the filler, volume fraction of PZT inclusions, temperature, frequency and micropores will affect the dielectric loss of the composite^{9, 22, 24, 28, 29, 30, 8, 32, 34}.

Increase in volume fraction of PZT increases the loss²². Increase in temperature decreases the dielectric loss^{9, 8, 32}. Increase in particle size increases the loss factor. Addition of dopant like carbon will increase the dielectric loss^{33, 34}. The $\tan \delta$ values for various composites are shown in Table 1.

3.2. PIEZOELECTRIC PROPERTIES

3.2.1. Piezoelectric charge(strain) coefficient d_{33} .

The theoretical equations predicting filler concentration dependent variation of effective piezoelectric charge(strain) coefficient is available in literature.

Furukawa equation⁵²

$$d_{eff} = \left[\frac{5c_2f}{(1-f)c_1 + (2+3f)c_2} \right] \left[\frac{3c_1d_2}{(2+f)\epsilon_1 + (1-f)\epsilon_2} \right] \rightarrow \quad (3)$$

Where f is the volume fraction of the ceramic inclusion, ϵ_1 , ϵ_2 represents the relative permittivity of the polymer and ceramic respectively and c_1 and c_2 are Young's moduli of the polymer and ceramic phases respectively, d_2 is the piezoelectric charge coefficient of the inclusion.

The parameters like particle size of the inclusion^{12, 22}, volumetric percentage¹⁹⁻²², temperature³⁸, poling methods^{16, 17, 27}, method of preparation^{19, 20} affects the piezoelectric strain coefficient of the composite. The d_{33} increases with the increase of volume fraction of the PZT inclusions^{19, 20, 21, 22, 25, 26, 33}, because PZT occupy dominant position of the contribution of electrical properties. Figure.3 shows the increase in the d_{33} with the increase of PZT volume percentage. Increase in PZT particle size increases the d_{33} of the composite^{12, 22, 35}, this is due to increase in particle size reduces the porosity. Wim Nhuapeng *et al.*²² reported that after increasing the volume of PZT over 65% he could not able to load the PZT particles with the size of $\sim 160\mu\text{m}$, he could not able to

load the PZT particles in the resin. However Safari *et al.*¹² reported that the bigger PZT particles in 0-3 composite had the tendency to yield higher d_{33} . Increase in the poling field increases the d_{33} of the composite³⁶. The increase in temperature will increase the piezoelectric charge coefficient³⁸. Sa Gang *et al.*³⁷ and Sakamoto *et al.*³² reported that addition of third phase like carbon will increase the piezoelectric properties of the composite. This is because of carbon particles could create continuous electrical flux path between the PZT grains. Amount of carbon in composite exceeds 1vol% the piezoelectric charge coefficient reduced because of the electrical conductivity has increased so much³². Table1 shows the piezoelectric charge coefficient values for different PZT- Polymer composites. Xiang-Dong Chen *et al.* reported relatively high d_{33} value 130pC/N for the PZT-PVDF composite²³.

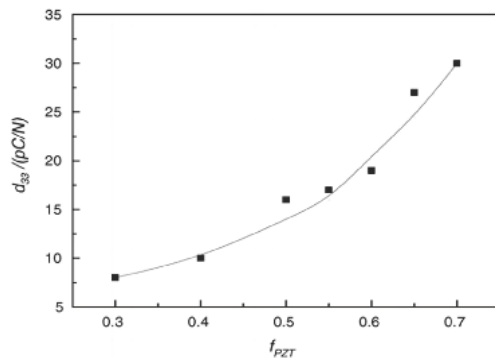


Figure.3 Piezoelectric strain coefficient, d_{33} , plotted as a function of PZT volume fraction in PZT-PVC composite³³.

3.2.2. Piezoelectric voltage coefficient.

Piezoelectric voltage coefficient g_{33} can be calculated using relative permittivity and piezoelectric charge coefficient d_{33} .

$$g_{33} = \frac{d_{33}}{\epsilon_0 \epsilon_r} \rightarrow \quad (4)$$

The g_{33} is proportional to d_{33} and inversely proportional to ϵ_r and ϵ_0 is the permittivity in vacuum. Changes in d_{33} will strongly affect the piezoelectric voltage coefficient. Increase in volume fraction of PZT inclusions will increase the piezoelectric voltage coefficient^{20,21,22,38}. Increment in dielectric constant is regular with increase of volume percentage of the filler. But the increment in d_{33} is reduced when the volume percentage attains 50%³⁵. This will affect the increment of piezoelectric voltage coefficient. However increase in filler volume fraction increases the piezoelectric voltage coefficient. Increase in the poling field increases the piezoelectric voltage coefficient³⁶. Table1 shows g_{33} values for different PZT-Polymer composites.

3.2.3. Piezoelectric Figure of Merit (FOM)_{piezo}

Piezoelectric figure of merit, $FOM_{piezo} = d_{33} \times g_{33}$. It depends on the increase in piezoelectric charge coefficient and dielectric constant. Figure of merit is considered for industrial applications purpose. Among all the composites, PZT-PVDF composite exhibit good piezoelectric figure of merits. Some composites have high figure of merit than the pure ceramics. Table.1. shows the piezoelectric figure of merit values for different PZT-Polymer composites.

4. CONCLUSION

This paper is purely a review study for PZT with different polymers of 0-3 connectivity. Among the various polymers

available for the composite, in this study only selected polymers have been chosen. The thorough study intended to select the following polymers PVDF, PVC, P(VDF-TrFE), PU, Epoxy, Polyester resin. All the polymers have been prepared by different methods which are not discussed here. The theoretical analysis reveals that the dielectric constant, piezoelectric strain coefficient and voltage coefficient increases with increase in volume percentage of PZT, temperature and particle size of PZT. Comparing to the composites made by PZT with other polymers, PZT-PVDF finds better for device quality sensors.

REFERENCES

1. D.P. Skinner, R.E. Newnham, and L.E. Cross, *Mater. Res. Bull.*, 13, 599 (1978).
2. T. R. Gururaja, W. A. Schulze, L. E. Cross, R. E. Newnham, B. A. Auld, and Y. J., Wang, *IEEE Trans. Sonics Ultrason.*, SU-32, 489 (1985).
3. P.M. Gehring, S. Wakimoto, Z.-G. Ye, and G. Shirane, *Phys. Rev. Lett.*, 87:27 277601/1 (2001).
4. Rui Zhang, Bei Jiang, and Wenwu Cao, *J. Appl. Phys.*, 90, 3471 (2001).
5. Y. P. Mao, S. Y. Mao, Z.-G. Ye, Z. X. Xie and L. S. Zheng, *J. Appl. Phys.* 108, 014102 (2010).
6. S. Wada, H. Yasuno, T. Hoshina, S.-M. Nam, H. Kakemoto, and T. Tsurumi, *Jpn. J. Appl. Phys.*, Part1 42, 6188 (2003).
7. T. Yamada, T. Ueda, T. Kitayama, *J. Appl. Phys.*, 53(6), 4328 (1982).
8. Walter K. Sakamoto, Darcy H.F. Kanda, D.K. Das-Gupta, *Mat Res Innovat* 5, 257 (2002).
9. D. K. Das-Gupta, M. J. Abdullah, *J. Mater. Sci. Lett.*, 7, 167 (1988).
10. R.E. Newnham, D.P. Skinner and L.E. Cross, *Mater. Res. Bull.*, 13, 525 (1978).
11. Lin H B, Cao M S, Yuan J, Wang D W, Zhao Q L and Wang F C, *Chin. Phys. B*, 17, 4323 (1988).
12. A. Safari, *J. Phys.* III, 4, 1129 (1994).
13. M. Dietze, J. Krause, C.-H. Solterbeck, and M. Es-Souni, *J. Appl. Phys.*, 101, 054113 (2007).
14. Ahmed S and Jones F R, *J. Mater. Sci.*, 25, 4933 (1990).
15. Tian S, Cui F and Wang X, *Mater. Lett.*, 62, 3859 (2008).
16. Dias C J and Das-Gupta D K, *IEEE Trans. Dielect. Electr. Insul.*, 5, 706 (1996).
17. C.J. Das, D.K. Dasgupta, *Key Eng. Mater.* 92–93, 217 (1994).
18. Matthias Dietze, Mohammed Es-Souni, *Sensors and Actuators A* 143, 329 (2008).
19. Zhang De-Qing, Wang Da-Wei, Yuan Jie, Zhao Quan-Liang, Wang Zhi-Ying and Cao Mao-Sheng, *Chin. Phys. Lett.*, 25[12], 4410 (2008).
20. E Venkatragavaraj, B Satish, P R Vinod and M S Vijaya, *J. Phys. D: Appl. Phys.*, 34 487 (2001).
21. B Satish, K Sridevi and M S Vijaya, *J. Phys. D: Appl. Phys.*, 35, 2048 (2002).
22. Wim Nhuapeng and Tawee Tunkasiri, *J. Am. Ceram. Soc.*, 85[3], 700 (2002).
23. Xiang-Dong Chen, Da-Ben Yang, Ya-Dong Jiang, Zhi-Ming Wu, Dan Li, Fu-Jun Gou, Jia-De Yang, *Sensors and Actuators A* 65, 194 (1998).
24. Dolly Sinha and P. K. C. Pillai, *J. Appl. Phys.*, 54 [5], 2571 (1988).
25. Kristin Arlt and Michael Wegener, *IEEE Trans. Dielect. Electr. Insul.*, 17[4], 1178 (2010).

26. Kar Lai Ng, Helen Lai Wa Chan, and Chung Loong Choy, *IEEE transactions on ultrasonics, ferroelectrics, and frequency control*, 47[6], 1308 (2000).
27. D.K. Das-Gupta and C. J. Dias, 6th Int. Cod. on Dielectric Materials, Measurements and Applications, DMMA6, Manchester, IEE, 393 (1992).
28. H. L. W. Chan, Y. Chen and C. L. Choy, *IEEE Trans. Dielect. Electr. Insul.*, 3[6], 800 (1996).
29. S. T. Lau, K. W. Kwok, F. G. Shin, and S. Kopf, *J. Appl. Phys.*, 102, 044104 (2007).
30. K. S. Lam, Y. W. Wong, L. S. Tai, Y. M. Poon, and F. G. Shin, *J. Appl. Phys.*, 96, 3896 (2004).
31. X.X. Wang, K.H. Wang, X.G. Tang, H.L.W. Chan, *Solid State Commun.* 130, 697 (2004).
32. W.K. Sakamoto, P. Marin-Franch, D.K. Das-Gupta, *Sensors and Actuators A* 100, 165 (2002).
33. Xiao-fang Liu, Chuan-xi Xiong, Hua-jun Sun, Li-jie Dong, Ri li, Yang Liu, *Mater. Sci. Eng. B* 127, 261 (2006).
34. LIU Xiaofang, XIONG Chuanxi, SUN Huajun, DONG Lijie, LI Rui, LIU Yang, *Journal of Wuhan University of Technology - Mater. Sci. Ed.* 20[4], 60 (2005).
35. Young Jun Choi, Myong-Jae Yoo, Hyung-Won Kang, Hyeung-Gyu Lee, Seung Ho Han and Sahn Nahm, *J. Electroceram*, 30, 30 (2013).
36. R. Senthilkumar, K. Sridevi, J. Venkatesan, V. Annamalai, and M. S. Vijaya, *Ferroelectrics*, 325, 121 (2005).
37. G. Sa-Gong, A. Safari, S.J. Jang, R.E. Newnham, *Ferroelectrics Lett.*, 5, 131 (1986).
38. X. F. Liu, H. J. Sun, C. X. Xiong, C. Y. Zhang, H. Zheng and M. Wei, *IEEE International Symposium on Applications of Ferroelectrics - ISAF*, doi:10.1109/ISAF.2009.5307545 (2009)
39. Pailyn Thongsanitgarn, Anucha Watcharapasorn and Sukanda Jiansirisomboon, *Surface Rev. Lett.*, 17[1], 1 (2010).
40. X. Cai, C. Zhong, S. Zhang, and H. Wang, *J. Mater. Sci. Lett.*, 16, 253 (1997).
41. S. B. Wang, T X Xu, J C Han, S Y Du., *Acta Mater. Comp. Sinica.*, 17[4],1 (2000).
42. A. Seema, K.R. Dayas, J.M. Varghese, *J. Appl. Polym. Sci.* 106[1], 146 (2007).
43. M.Olszowy, *Cond. Matter Phys.*, 6, 307 (2003).
44. R. Fries and A. J. Moulson, *J. Mater. Sci.: Mater. Electron.*, 5, 238 (1994).
45. K. A. Hanner, A. Safari, R. E. Newnham, and J. Runt, *Ferroelectrics*, 100, 255 (1989).
46. W. K. Sakamoto, S. Kagesawa, D. H. Kanda, D. K. Das-Gupta, *J. Mater. Sci.* 33, 3325 (1998).
47. R. Zeng, K. W. Kwok, H. L. W. Chan, and C. L. Choy, *J. Appl. Phys.* 92[1], 2674 (2002).
48. J. L. Yao, C. X. Xiong, L. J. Dong, C. Chen, Y. A. Lei, L. Chen, R. Li, Q. M. Zhu and X. F. Liu, *J. Mater. Chem.*, 19, 2817 (2009).
49. A. S. Bhalla, R. E. Newnham, L. E. Cross, and W. A. Schulze, *Ferroelectrics*, 33 139 (1981).
50. S. Banerjee, W. Du, L. Wang, K. A. Cook-Chennaul, *J Electroceram*, doi:10.1007/s10832-013-9834-8
51. Bai W and Yang D, *Ferroelectrics*, 157, 427 (1994).
52. T. Furukawa, *IEEE Trans. Electron. Insulat.*, 24, 390 (1989).